



Spectroscopic Analysis of Fire Suppressants and Refrigerants Using Laser-Induced Breakdown Spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is evaluated as a means of detecting the fire suppressants CF_3Br (Halon 1301), $\text{C}_3\text{F}_7\text{H}$ (FM-200), CF_4 (Halon 14), and the refrigerant $\text{C}_2\text{F}_4\text{H}_2$ (HFC-134a). The feasibility of employing LIBS for time- and space-resolved measurement of these agents during use, storage, and recharge is discussed. Data that demonstrate the conditions necessary for optimal detection of these chemicals are presented.

Acknowledgments

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1. Introduction

Certain halogenated hydrocarbons (halons), such as Halon 1301 (CF_3Br) and Halon 1211 (CF_2ClBr), are among the most effective fire suppressants. Unfortunately, the production of these Br-containing fire suppressants has been banned by international agreement [1] because they have been implicated as contributing to stratospheric ozone depletion. Part of the ongoing effort of choosing a replacement suppressant is determining how a given suppressant is dispersed within a clutter-filled environment (such as the crew compartment aboard a military vehicle) and how the concentration of suppressant changes with time after being released. Also, there is great interest in developing field sensors for monitoring unwanted release (leaks) of these chemicals.

Many candidate replacement suppressants are fluorinated hydrocarbons [2]. In an initial study, we have used laser-induced breakdown spectroscopy (LIBS) to measure atomic F emission from candidate replacement suppressants (CF_4 , CF_3H , CF_2H_2 , and $\text{C}_2\text{F}_5\text{H}$) [3]. These measurements were used to deduce limits of detection (LODs) for these compounds. The reason for choosing LIBS for these measurements is because the technique allows laser delivery and collection optics to be fiber-coupled so that remote and/or hostile environments can be accessed, as well as the fact that the data collection rate is determined by the repetition rate of the laser. This means that LIBS-based measurements of suppressant concentrations may be made rapidly and in situ during full-scale fire-suppressant testing or for detection of leaks from storage containers. Although there are commercially available halocarbon (refrigerant) detectors that use detection techniques other than ultraviolet (UV)-visible plasma emission, there is still a need for a halocarbon sensor with certain desirable characteristics such as near real-time response, remote operation, and freedom from other chemical interferences.

The work presented here extends our initial study in two important directions. First, it includes three important not previously studied compounds: (1) Halon 1301 (CF_3Br), (2) FM-200 ($\text{C}_3\text{F}_7\text{H}$, a leading replacement candidate for fire suppression), and (3) HFC-134a ($\text{C}_2\text{F}_4\text{H}_2$, a common replacement refrigerant). Second, unlike the initial study, where we

captured the LIBS spectra using a monochromator/PMT system, in this study, we concentrate on using and systematically optimizing the photodiode array/spectrograph system for the purpose of utilizing it in real-world applications.

2. Background

LIBS is a well-established technique [4] and has been widely discussed in the literature. Briefly, a pulsed laser beam is focused to a fluence of approximately 10^8 to 10^9 W/cm² on or in the sample. In this focal region, dielectric breakdown of the sample occurs. Continuum absorption of the laser radiation by free electrons produced during the dielectric breakdown further ionizes and heats the sample, generating the plasma by cascade ionization. The emission of the atomic and molecular constituents, which are excited within the plasma, is collected with lenses or fiber optics, spectrally resolved, and measured using a photomultiplier or optical multichannel analyzer. Typical LIBS plasma temperatures are in the 20,000 to 25,000 K range for gases at atmospheric pressure [5].

Although LIBS is most commonly employed for solids analysis [6, 7] (such as measurement of metal contamination of soils, paint, metals, and steels), early work [8] demonstrated the feasibility of the technique for detection of F-containing species. Additionally, LIBS analysis of gaseous samples has been reported for the detection of Cl, F, S, P, As, and Hg in air [9–11]. Recently, our laboratory employed LIBS to determine LODs for a series of fluorinated methanes (CF₄, CF₃H, and CF₂H₂) [3].

In this report, we use optical fibers to collect radiation emitted by the laser and then transfer it to the monochromator. Optical fibers have been utilized by other researchers for the remote analysis of metals in the environment [12, 13]. They have also been used in a probe arrangement for both transfer of the plasma-generating pulse and the collection of emitted radiation [14].

3. Experimental

A schematic of the experimental apparatus is shown in Figure 1. Laser radiation at a wavelength of $1.06\ \mu\text{m}$ is supplied by an Nd:YAG laser (Quanta-Ray DCR2A). The laser repetition rate is 10 Hz. The laser radiation is passed through a 25-mm-diameter planoconvex lens with a focal length of 50 mm and is brought to a focus 2 mm above the outlet port of the flow apparatus used to deliver the analyte. Plasma emission is collected using an $f/4$ quartz lens, collimated, and focused directly into a 1-mm-aperture bifurcated optical-fiber bundle consisting of 10 individual fibers in a cylindrical shape at the light collection point and a rectangular configuration at the other end. The output from the optical-fiber bundle is spectrally resolved using a spectrograph (Jarrell-Ash Monospec 27) and measured using an intensified photodiode-array detector (Princeton Instruments, IRY1024G). The grating is used in first order, and the effective resolution is around 0.7 nm. Single-shot spectra were obtained for each of these measurements. All spectra were obtained in a single-shot manner.

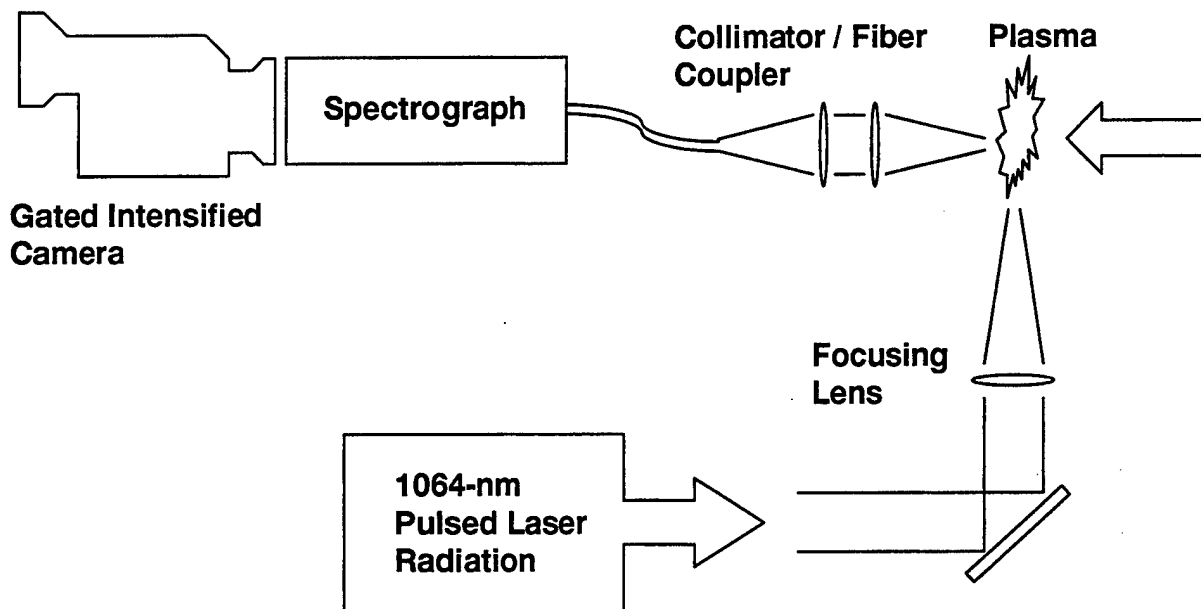


Figure 1. Instrumentation Diagram.

The sample delivery device has been described previously [15]. The device consists of 0.125-in (outside diameter [o.d.]) stainless-steel tube placed inside a 0.375-in (o.d.) stainless-steel tube. Analyte gas is delivered by the center tube at a flow rate of 50 standard cubic centimeters per minute (sccm). The outer tube delivers Ar gas flowing at 500 sccm. The Ar gas is used as a sheath to confine analyte to the focal volume of the laser. The sample delivery device was mounted on a three-dimensional stage in order to adjust the location of the analyte stream relative to the laser focal volume. For LOD studies described here, the analyte sample was mixed with ultrapure N. Gas flows were controlled by mass flow meters (Tylan). All gases were supplied by Matheson, Inc., and were used without further purification. The mass flow controllers were calibrated using a wet test meter.

4. Results and Discussion

In general, initial laser-induced plasma emission consists of continuum radiation for several hundred nanoseconds [4]. This continuum emission is typically much more intense than atomic and molecular emission, which occur sequentially from one to several microseconds following plasma formation. Figure 2 shows typical time-resolved laser-induced breakdown spectra for neat CF_3Br with an Ar sheath gas. Visible in this LIBS spectrum are emission lines from F and Ar.

Figure 3 illustrates the spectral emission from neat CF_3Br . This figure shows the Br emission lines in the 460- to 480-nm wavelength region. All spectra obtained for the compounds of interest were identical except in this region. For these studies, the F emission line at 685.6 nm ($3\text{S}^4\text{P}_{5/2} - 3\text{P}^4\text{D}_{7/2}^0$) is used for signal optimization and signal-to-noise calculations. This line was chosen because it is the strongest F emission line in this spectral region [3] and because it is free from interferences from O, N, and Ar. For optimum sensitivity, it is necessary to minimize the contribution to the signal from the continuum radiation, while maximizing analyte signal-to-noise ratio. The factors that must be considered in achieving this are discussed next.

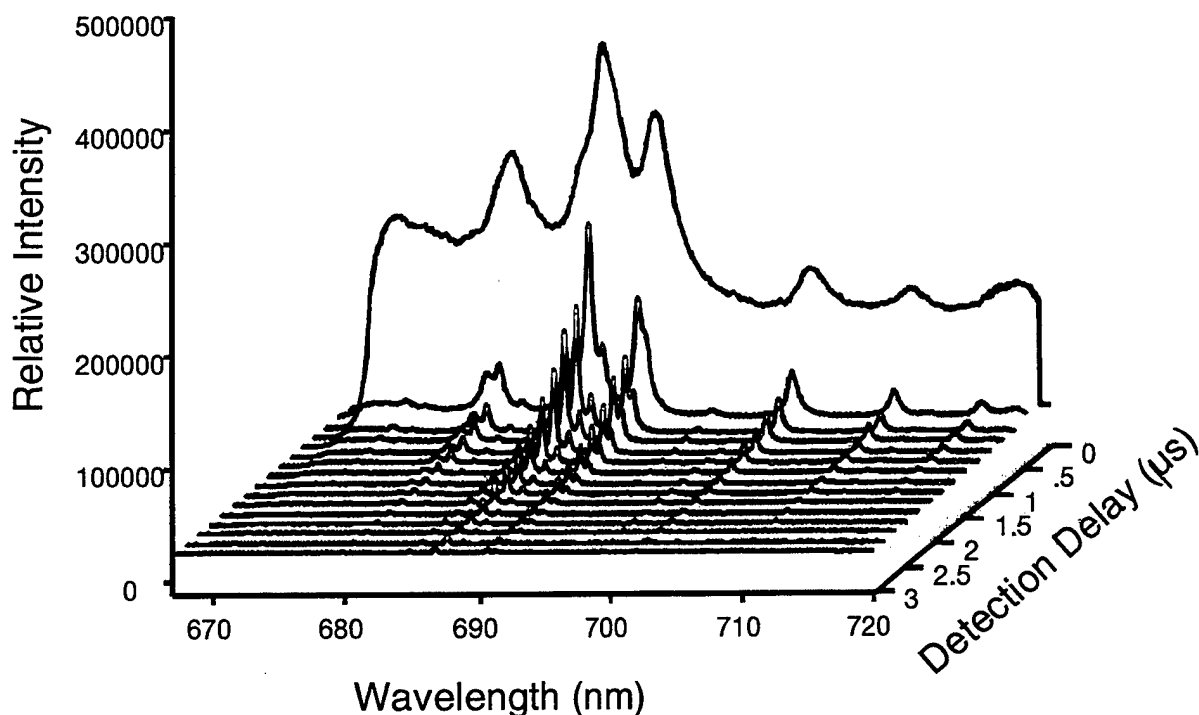


Figure 2. Time Delay Spectra, Neat Halon 1301, Integration Time ($0.2\ \mu\text{s}$), Gate Delay Varied From 0.0 to $3.0\ \mu\text{s}$ in $0.2\text{-}\mu\text{s}$ Steps.

4.1 Optimization of Gate Delay. Previous studies of F emission from halocarbons [3] delayed signal collection by $2\ \mu\text{s}$ after the laser pulse. Since the time that the diode array detector intensifier is on is termed “gate width,” the delay between the laser firing and collection of signal is called “gate delay.” For these studies, the signal-to-noise ratio for emission from the atomic F line at $685.6\ \text{nm}$ was measured as a function of gate delay for an incident laser power of $60\ \text{mJ}$ per pulse. Integration time (i.e., the gate width) was $0.5\ \mu\text{s}$. Figure 4 shows that, for the compounds studied here, the optimum gate delay was $0.6\ \mu\text{s}$. The uncertainty of the data shown in Figure 4 is approximately 15%. We have found that the uncertainty level for all the data we report in this work is in the 15–20% range. The signal-to-noise ratios for all experiments were calculated from the average of 5 peak measurements and the root mean squared (rms) noise from 20 blank measurements.

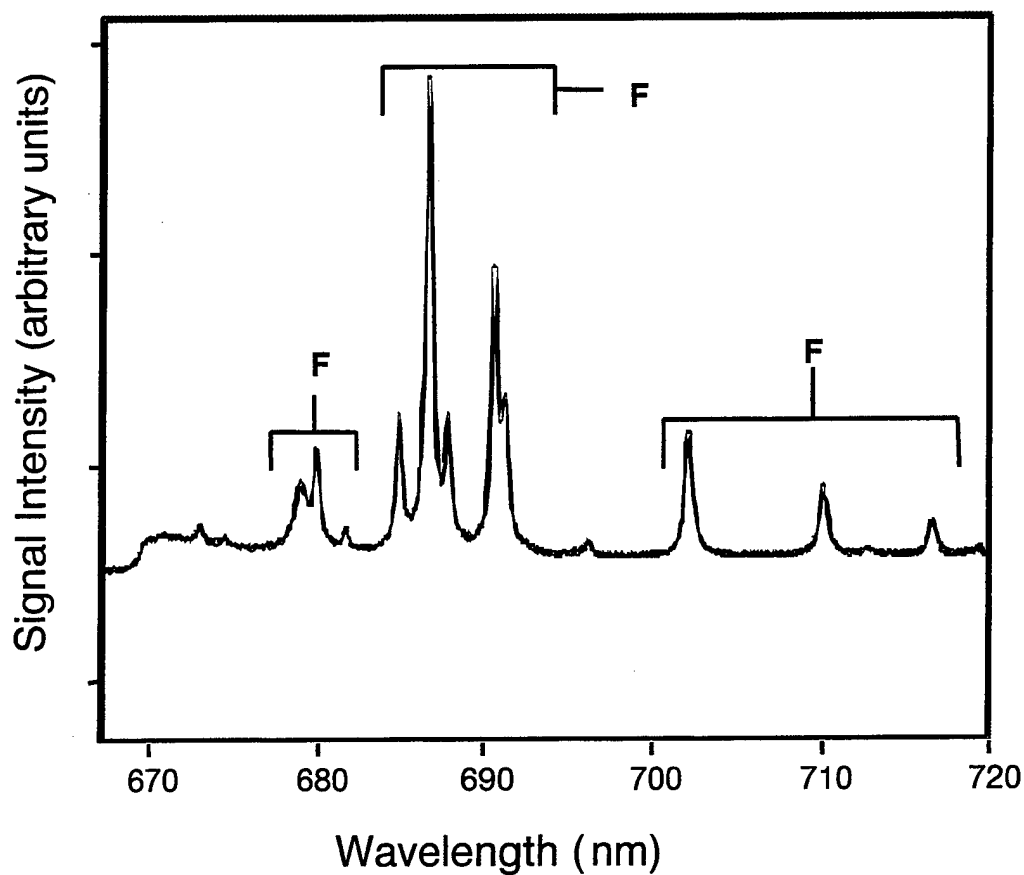
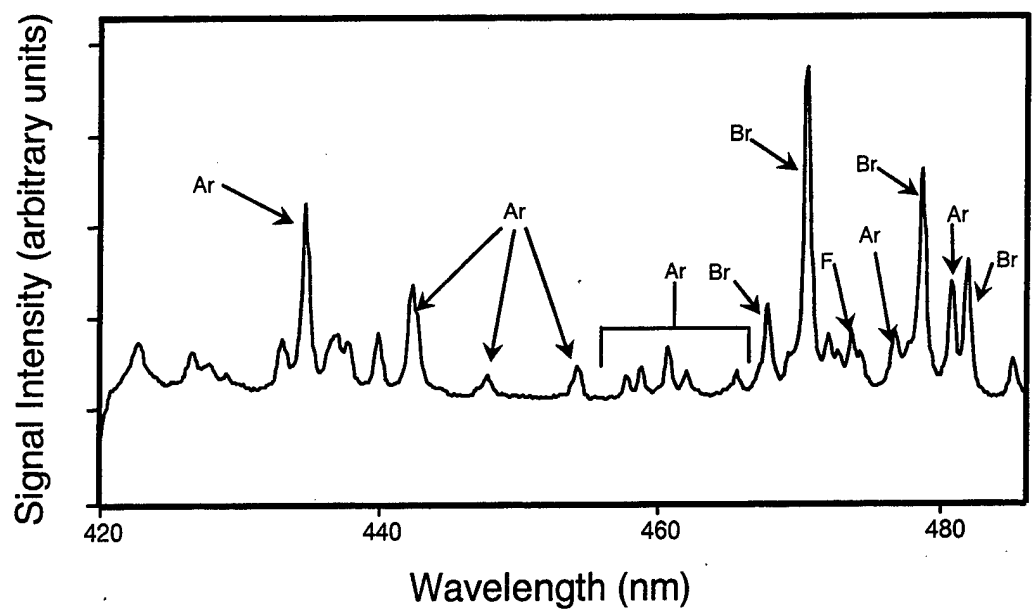


Figure 3. The LIBS Spectrum of CF₃Br (Halon 1301).

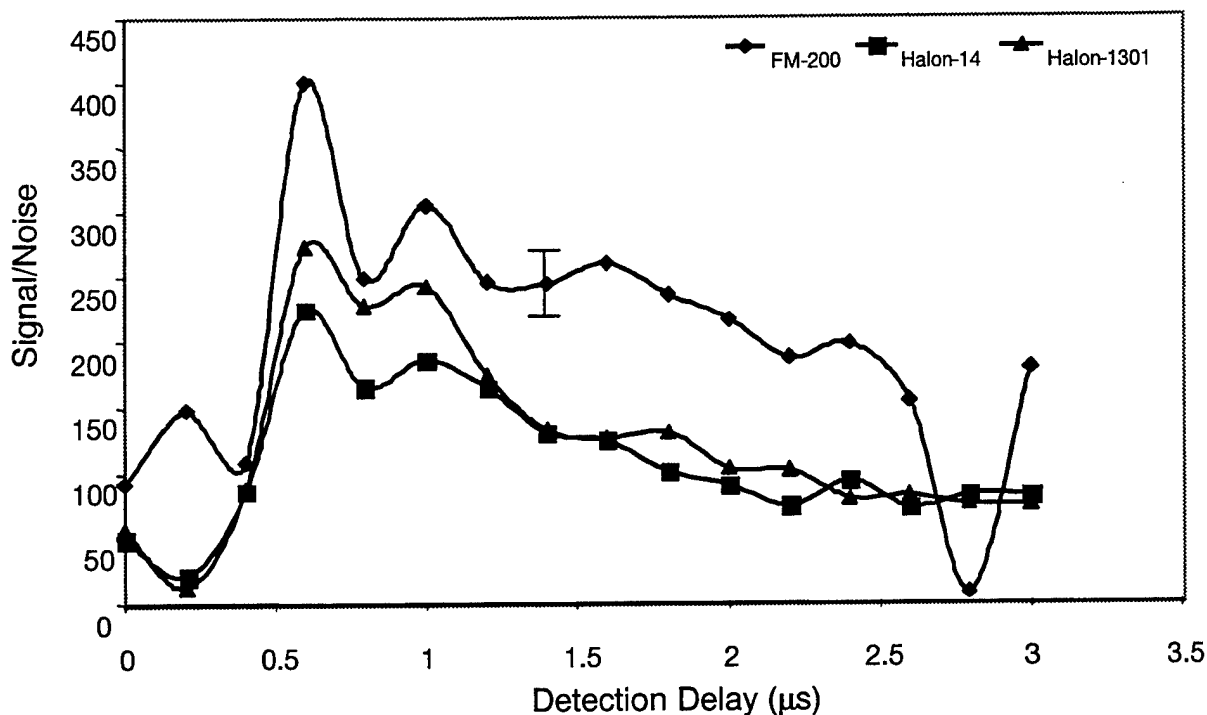


Figure 4. Signal-to-Noise Ratio for Atomic F Emission at 685.6 nm as a Function of Gate Delay for the Gated, Intensified Diode Array Detector Used in These Studies. For Each of the Compounds Studied, Optimum Delay Was Determined to Be 0.6 μ s.

4.2 Signal-to-Noise Ratio Dependence on Laser Power. The emission intensity from a plasma occurring in an N/C_3F_7H gas mixture containing 4.23 parts per thousand (ppTh) of C_3F_7H was measured at various laser pulse energy levels to determine the laser power that maximized the signal-to-noise ratio for emission from atomic F at 685.6 nm. Table 1 shows that, for C_3F_7H , the laser pulse energies that yield the best signal-to-noise ratio for F emission were observed at 60 mJ per pulse and 100 mJ/pulse. A pulse energy of 60 mJ/pulse was chosen for further optimization studies since we observed that, at greater than approximately 80 mJ/pulse, the plasma appeared to be breaking apart/segmenting. This is a well-known phenomenon in the laser breakdown field, where, at sufficiently high laser pulse energy, the single microplasma converts into multiple spatially distinct microplasmas.

4.3 Optimization of Gate Width. To determine the optimum signal integration time (gate width), the signal-to-noise ratio for atomic F emission at 685.6 nm was measured as a

Table 1. The Dependence of Signal-to-Noise Ratio on Laser Energy for Atomic F Emission at 685.6 nm

Energy (mJ/Pulse)	Signal to Noise
40	229
50	247
60	251
72	157
80	119
90	231
100	245
110	209
120	184

function of gate width for a plasma formed in 4.23 ppTh FM-200 in N. Laser power was 60 mJ per pulse, and the gate delay was 0.6 μ s. The gate width was varied from 0.2–20 μ s. Figure 5 shows that no further improvement in signal-to-noise ratio for F emission was achieved for gate widths greater than 2.5 μ s. Further studies indicated that the lowest (i.e., most sensitive) LODs were found to be at a gate width of 0.5 μ s.

4.4 LOD. LODs were determined using

$$\text{LOD} = \frac{3 * S_b}{m} , \quad (1)$$

where S_b is the standard deviation of 20 background measurements and m is the slope of the signal intensity vs. concentration calibration curve. LOD is the level at which it is possible to conclude that the analyte is present. In Table 2, we find that FM-200 exhibits the lowest LOD (170 ppm), while the highest was that of Halon 1301 (LOD = 750 ppm).

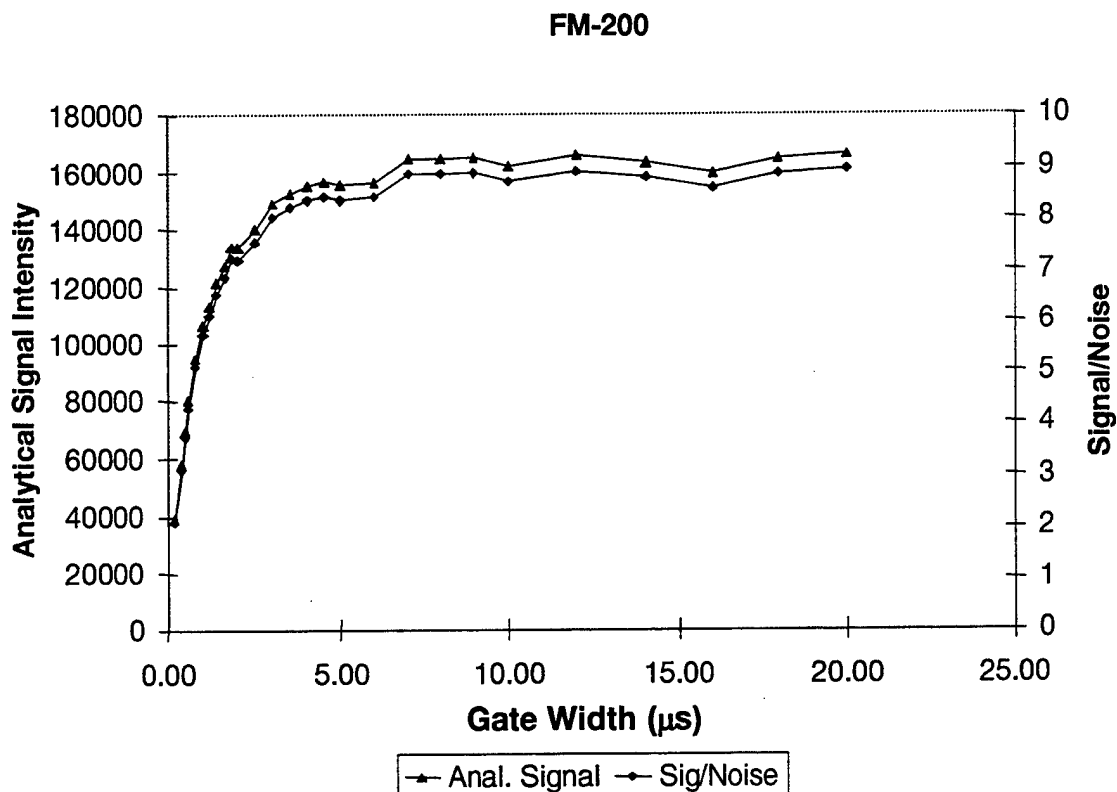


Figure 5. Signal-to-Noise Ratio Dependence on Integration Time.

Table 2. LODs for Halon Alternatives Examined for This Study

	Halon 14 ^a	Halon 1301 ^a	FM-200 ^a	HFC-134a
$y = mx + b$				
m (slope)	2.080	1.721	3.313	1.118
b (y-intercept)	42114	41156	37228	35217
R^2	0.9990	0.9730	0.9842	0.9988
LOD ^b (ppm)	490	750	170	530

^a n = 5.

^b 20 background measurements.

Figure 6 shows LIBS atomic F emission intensity at 685.6 nm vs. concentration for all four compounds studied. Correlation coefficients for these calibration curves are listed in Table 2.

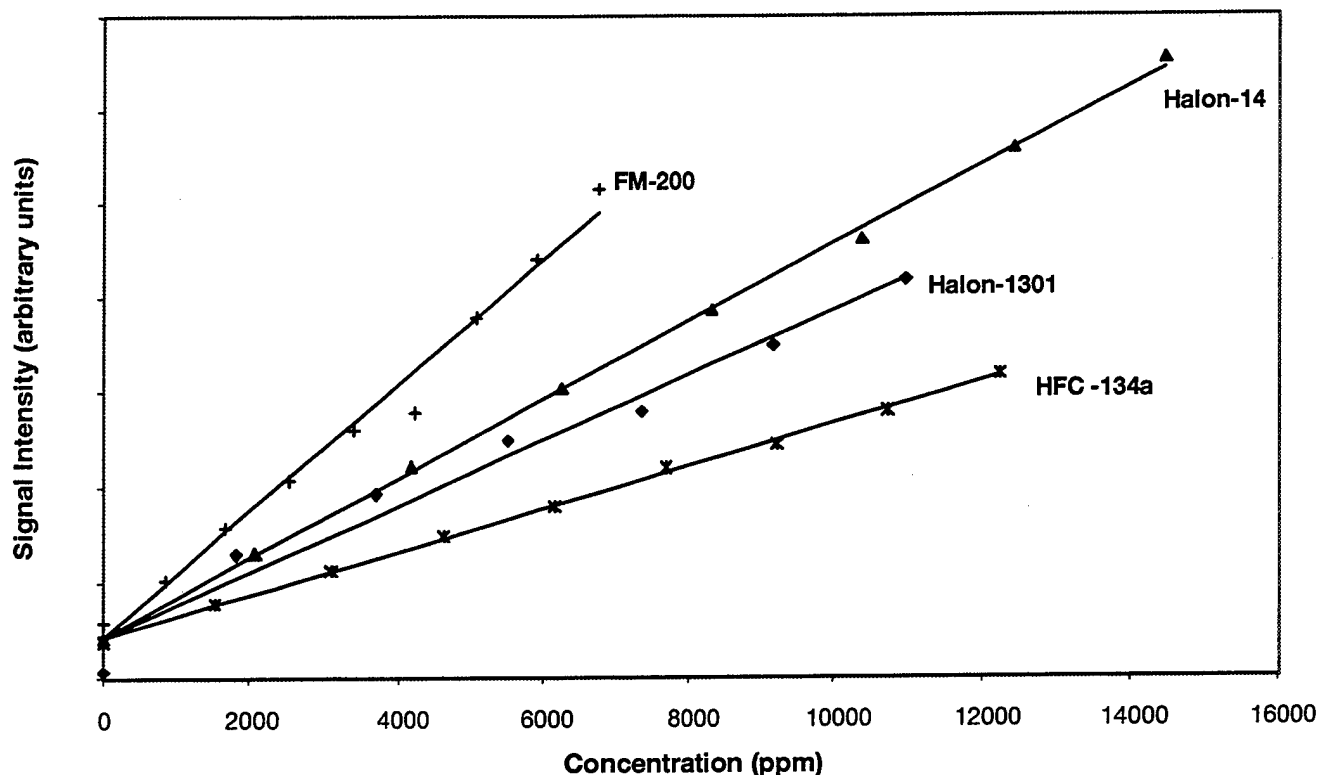


Figure 6. Concentration vs. LIBS Atomic F Emission Intensity for the Four Compounds Analyzed for This Study.

Figure 7 shows the single-shot LIBS spectrum of CF_3Br (9.16 ppTh) measured over the spectral region from 670–720 nm. As stated before, the spectra for all compounds were identical in this spectral region, indicating that identification of the parent molecule from LIBS spectra measured over this spectral region is not feasible, although such identification is not necessary for our applications. This spectrum indicates that the LIBS detector should be useful for real-time concentration measurements, in full-scale fire-suppression tests, where the required sensitivities are in the 1–100-ppTh range.

5. Conclusion

This paper demonstrates the wide applicability of the LIBS technique to measure concentrations of a new generation of fire-extinguishing agents and refrigerants. To the best of

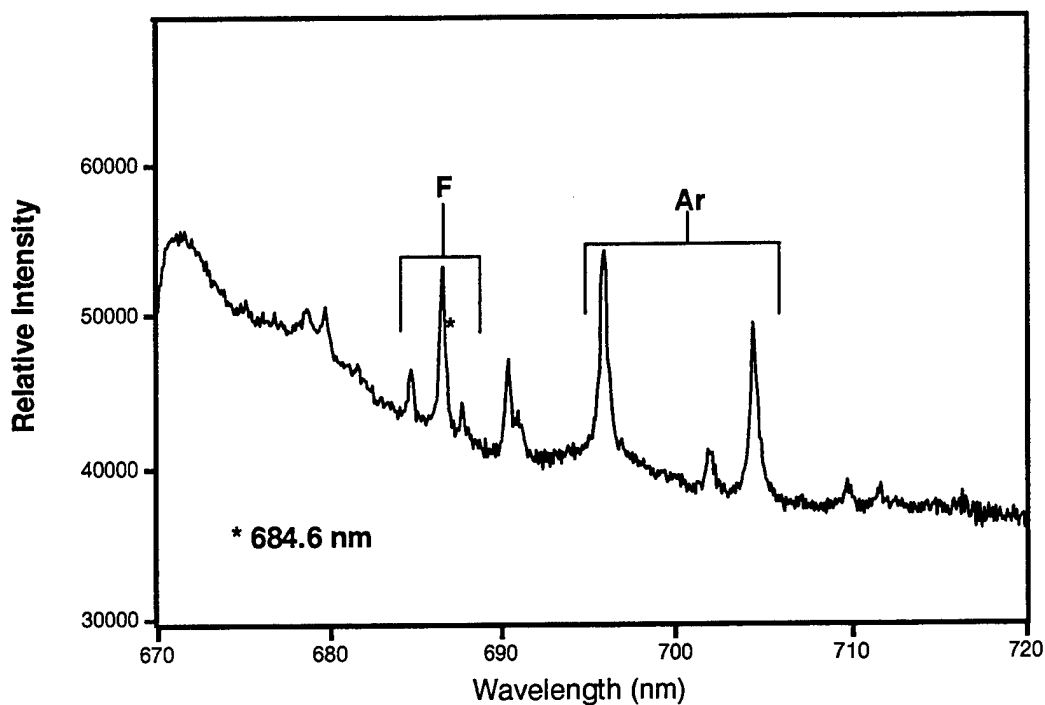


Figure 7. Single-Shot Halon 1301 Spectrum, 9.17 ppTh, 0.6- μ s Detection Delay, 0.5- μ s Integration Time.

our knowledge, we present the first quantitative LIBS spectra of CF_3Br , $\text{C}_3\text{F}_7\text{H}$, and $\text{C}_2\text{F}_4\text{H}_2$, which are all commercially and environmentally important compounds. LODs for these halocarbons are somewhat greater (less sensitive) than those previously reported for fluorocarbons. We believe this decrease in sensitivity is caused by the use of fiber optics to collect the LIBS radiation, as well as by the use of a linear diode array to measure the LIBS emissions. This loss in sensitivity, relative to lens-coupled systems that use photomultiplier tubes for detection, is compensated by the ability of the present system to make measurements in hostile and remote environments.

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